

# STARKIST SAMOA EFFLUENT PRIORITY POLLUTANT ANALYSIS: JUNE 2012 SAMPLING

Prepared For: StarKist Samoa

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## **Purpose**

This memorandum presents the results of the effluent priority pollutant analysis conducted for StarKist Samoa. The effluent sampling and analysis is required under StarKist Samoa's NPDES Permit (No. AS 0000019). The analyses were conducted using a 24-hr composite effluent sample collected in June 2012.

# Background

StarKist Samoa must monitor treated wastewater effluent as required in its NPDES Permit, Part II, Section B. The effluent monitoring results presented in this Technical Memorandum meet the requirements of NPDES Permit Section B.1 (Priority Toxic Pollutants Scan), which is stated as follows:

In accordance with federal regulations, the permittee shall conduct a Priority Toxics Pollutants scan during the fourth or fifth year of the five-year permit term to ensure that the discharge does not contain toxic pollutants in concentrations that may cause a violation of water quality standards. The permittee shall perform all effluent sampling and analyses for the priority pollutants scan in accordance with the methods described in the most recent edition of 40 CFR 136, unless otherwise specified by EPA. 40 CFR 131.36 provides a complete list of Priority Toxic Pollutants.

## Sampling Location

The effluent sampling location is the NPDES permit established sampling point and the same as used when StarKist Samoa is sampling effluent for other tests such as the semi-annual bioassay sampling and routine discharge monitoring. It is located just downstream of the Parshall flume, prior to discharge into the joint cannery outfall.

# Effluent Sampling Methods

Between 1200 (noon) on 5 June 2012 and 0900 on 6 June 2012, a 24-hour flow-weighted composite sample of final effluent was collected from the StarKist Samoa effluent discharge. Detailed sampling procedures are described in the previously established SOP for cannery effluent sampling for toxicity and chemistry testing.

At each sampling time samples were collected into three 1-litre amber glass bottles. Volatile organic samples were collected into two individual vials at each sampling time. The samples were stored on ice, or in a refrigerator, until completion of the 24-hour sampling period. After all samples were collected a flow-proportioned composite sample was prepared. The grab sample collection times, effluent flow rates, and the relative effluent flow volumes calculated from plant flow records are summarized in Table 1. The relative effluent flow volumes were used to prepare the final composite sample, which was used to fill the various sample containers (except for the volatile organic samples¹).

The sample containers were packed on ice, in an ice chest, for shipment to the laboratory. A chain-of-custody form for the samples were completed and sealed into a zip-lock bag and taped inside the lid of the ice chest. The samples were shipped via DHL to the testing laboratory. The chain-of-custody form is provided in Attachment 1.

# Effluent Sampling Results

The results of the effluent sample analysis for priority pollutants are given in Tables 2 through 6. Table 7 provides the data qualifiers for this data set. Detailed laboratory analytical results are provided in Attachment 1. Results are presented in terms of the data types: general inorganics and nutrients, metals, organochlorine pesticides and PCB's, volatiles, and semi-volatiles, in Tables 2 through 6, respectively. Ammonia, total Kjeldahl nitrogen (TKN), total phosphorous, oil & grease, mercury, copper, and zinc were not analyzed because these parameters are routinely sampled and tested as required by the permit and reported on the routine discharge monitoring reports (DMRs). Results are

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<sup>&</sup>lt;sup>1</sup> One volatile organic sample, the duplicate collected at the same time, and one of three trip blanks, were selected at random by the laboratory for testing.

compared to the United States Environmental Protection Agency (USEPA) criteria<sup>2</sup> and the American Samoa Environmental Protection Agency (ASEPA) criteria<sup>3</sup>.

#### Conventional Constituents

With the exception of cyanide (free and total) there were detected values reported for all constituents in the general category (Table 2). As mentioned above, constituents normally monitored and reported in the monthly DMRs were not included in the priority pollutant scan. With the exception of sulfide there are either no USEPA criteria or ASEPA criteria or the criteria is not for saltwater.

The USEPA criterion for sulfide is  $2.0~\mu g/l$  (saltwater criteria continuous concentration [CCC]). This criterion is in terms of *undissociated* sulfide (H<sub>2</sub>S). The effluent analysis resulted in a value of  $3.0~\mu g/l$  as *total* sulfide. The fraction of total sulfide that is undissociated depends on temperature, pH, and ionic stregnth (salinity). Using the minimum permitted limitation for pH, and typical values for effluent temperature and effluent salinity<sup>4</sup>, the undissociated sulfide in the sample is approximately equal to the NRWQC criterion. It is noted that the sulfide will be reduced to nondetectable levels immediately after discharge from the diffuser (within one second). Based on the above discussion it was not considered necessary to reanalyze for sulfide.

#### Metals

The effluent sample results for metals indicates that twelve metals were detected as present, aluminum, arsenic, barium, boron, cadmium, iron, magnesium, manganese, molybdenum, nickel, selenium, and silver (Table 3). With the exception of arsenic, the metal values measured for this analysis did not exceed applicable criteria. Selenium and silver were reported at estimated values between the method reporting limit (MRL) and the method detection limit (MDL). It is noted that copper, zinc, and mercury are monitored and reported in routine semi-annual effluent testing and were not included in the priority pollutant scan.

The ASWQS criterion for arsenic is  $10 \,\mu g/l$  and the reported value was  $16.1 \,\mu g/l$ . However, it was suspected that the arsenic value was inaccurate because of interferences from the seawater (thaw water) in the effluent. Therefore arsenic was retested during the August 2012 semi-annual effluent toxicity testing<sup>5</sup>, using a more appropriated analytical method,

 $<sup>^2</sup>$  The latest version (November 7, 2012) of the USEPA National Recommended Water Quality Criteria (NRWQC) was used as required by the American Samoa Water Quality Standards (ASWQS) for those parameters not specifically listed with numerical criteria in the ASWQS.

<sup>&</sup>lt;sup>3</sup> The ASWQS criteria were used if specific numerical criteria are listed.

<sup>&</sup>lt;sup>4</sup> StarKist Samoa uses seawater for thaw water and the effluent is therefore partly seawater.

<sup>&</sup>lt;sup>5</sup> The laboratory data are provided in the August 2012 toxicity testing report currently in preparation.

and the result was 1.31  $\mu$ g/l, well below the ASWQS criterion. No additional testing is considered necessary.

# Organochlorine Pesticides and PCB's

The effluent sample test results indicate no constituents in this category were detected.

## Volatile Organics and Semi-Volatile Organics

Volatile organics analysis of the effluent sample indicated that two constituents, toluene and benzene, were detected at *estimated* concentrations of 0.14  $\mu$ g/l and 0.080  $\mu$ g/l, respectively (Table 5). NRWQC criteria (for human health) were not exceeded for these two constituents. All other constituents were reported as not detected.

The semi-volatile analysis results (Table 6) for the effluent sample reported one constituent detected above the method reporting limit and two constituents estimated between the MRL and the MDL. Phenol was reported at 220  $\mu g/l$ , which is well below NRWQC criterion for human health. Diethyl phthalate and Bis(2-ethylhexyl) phthalate were *estimated* at 0.43  $\mu g/l$  and 1.2  $\mu g/l$ , respectively. These values are below (diethyl phthalate) or equal to (bis(2-ethylhexyl) phthalate) the NRWQC for human health. No additional testing is considered necessary for these parameters.

#### Dioxin

Dioxin (2,3,7,8-TCDD) was analyzed and reported as not detected. The MRL was 10.4 pg/l and the EDL was 1.23 pg/l. The criterion for dioxin was not exceeded.

Table 1 StarKist Samoa Effluent Composite Worksheet for the June 2012 NPDES Priority Pollutant Chemistry Samples								
Grab Sample No.	Sample Collection Time		Flow (mgd)	Fraction of Total Flow	Volume of Sample Used for Composite			
	Date	Time			(ml)			
1	6/5/12	1200	1.66	0.1301	1967			
2	6/5/12	1500	1.67	0.1305	1974			
3	6/5/12	1800	1.44	0.1129	1706			
4	6/5/12	2100	1.47	0.1152	1742			
5	6/6/12	0000	2.06	0.1610	2435			
6	6/6/12	0300	1.75	0.1372	2075			
7	6/6/12	0600	1.24	0.0973	1472			
8	6/6/12	0900	1.48	0.1152	1746			
		Totals:		1.0000	15120			

Table 2
StarKist Samoa Effluent Priority Pollutant Conventional Constituents Analysis
June 2012

			_	_					
Constituent	Result	Result Notes (see Table 7)		Dilution Factor	Method Reporting Limit	Method Detection Limit	Extraction Method	Analysis Method	
Bromide	16.6	=		50	5.0	0.2		300.0	
Fluoride	18	=		50	10	0.2		300.0	
Sulfate	639	=		100	20	1		300.0	
Sulfide	3.0	*		1	2.0	0.4		SM4500-S2-F	
Sulfite	16.8	Н		1	2.0	0.3		SM4500-SO32-B	
Cyanide, free	ND	U		1	0.010	0.010		9014	
Cyanide, total	ND	U	mg/l	1	0.0047	0.0009	N/A	SM4500-CN-E	
Chemical Oxygen Demand	590	=		10	50	30		SM5220C	
MBAS	0.188	*		1	0.050	0.050		SM5540C	
Phenolics, Total	0.385=			1	0.010	0.004		420.1	
Carbon, Total Organic	175 =			50	25	4		SM5310C	
Nitrate+Nitrite as Nitrogen	0.265	=		1	0.050	0.009		353.2	
Color	75	=	Co-Pt units	5	25	25		SM2120B	

Table 3								
StarKist S	StarKist Samoa Effluent Priority Pollutant Metals Analysis  June 2012							
Constituent	Result	Result Notes (see Table 7)	Units	Dilution Factor	Method Reporting Limit	Method Detection Limit	Extraction Method	Analysis Method
Aluminum	791	=		1	50.0	2.0		6010C
Antimony	3.0	U, N		1	10.0	3.0		6010C
Arsenic	16.1	=		1	10.0	4.0		6010C
Barium	3.1	=		1	2.0	0.4		6010C
Beryllium	0.09	U		1	0.20	0.09		6010C
Boron	1110	=		1	10.0	2.0		6010C
Cadmium	1.3	=		1	0.5	0.3		6010C
Chromium	0.6	U		1	2.0	0.6		6010C
Cobalt	0.4	U		1	1.0	0.4		6010C
Iron	231	=	/1	1	10.0	3.0	N/A	6010C
Lead	4.0	U	μg/l	1	10.0	4.0	IN/A	6010C
Magnesium	372000	=		1	20.0	2.0		6010C
Manganese	10.8	=		1	0.6	0.2		6010C
Molybdenum	3.4	=		1	2.0	0.6		6010C
Nickel	3.3	=		1	2.0	0.7		6010C
Selenium	12.3	J, N		1	20.0	5.0		6010C
Silver	1.0	J		1	2.0	0.7		6010C
Thallium	2.0	U		1	10.0	2.0		6010C
Tin	2.0	U		1	10.0	2.0		6010C
Titanium	0.4	U		1	1.0	0.4		6010C

Table 4									
	StarKist Samoa Effluent Priority Pollutant								
Organochlorine Pesticides and Polychlorinated Biphenyls Analysis									
	June 2012								
Constituent	Result	Result Notes (see Table 7)	Units	Dilution Factor	Method Reporting Limit	Method Detection Limit	Extraction Method	Analysis Method	
alpha-BHC	ND	U, *		50	0.50	0.033			
beta-BHC	ND	U, *		50	0.50	0.040			
gamma-BHC									
(Lindane)	ND	U, *		50	0. 50	0.10			
delta-BHC	ND	U, *		50	0.50	0.18			
Heptachlor	ND	U, i, *		50	0.77	0.77			
Aldrin	ND	U, i, *		50	2.2	2.2			
Heptachlor Epoxide	ND	U, *		50	0.50	0.050			
Endosulfan I	ND	U, *		50	0.50	0.065			
Dieldrin	ND	U, *		50	0.50	0.043			
4,4'-DDE	ND	U, *		50	0.50	0.055			
Endrin	ND	U, *		50	0.50	0.065			
Endosulfan II	ND	U, *		50	0.50	0.050			
4,4'-DDD	ND	U, *	μg/l	50	0.50	0.075	3520C	608	
Endrin Aldehyde	ND	U, *		50	0.50	0.085			
Endosulfan Sulfate	ND	U, *		50	0.50	0.060			
4,4'-DDT	ND	U, *		50	0.50	0.090			
Toxaphene	ND	U, *		50	25	4.2			
Chlordane	ND	U, *		50	9.9	1.1			
Aroclor 1016	ND	U, *		50	2.5	2.2			
Aroclor 1221	ND	U, *		50	5.0	2.9			
Aroclor 1232	ND	U, *		50	5.0	2.5			
Aroclor 1242	ND	U, *		50	5.0	0.90			
Aroclor 1248	ND	U, *		50	5.0	1.8			
Aroclor 1254	ND	U, *		50	5.0	1.5			
Aroclor 1260	ND	U, *		50	5.0	2.7			

# Table 5 **StarKist Samoa Effluent Priority Pollutant** Volatile Organic Analysis, June 2012 (Duplicate Samples Analyzed - Identical Results)

(Duplicate	Campi	ics Allaly.	zeu - luei	ilicai i i	iesuits)			
Constituent		Result Notes (see Table 7)	Units	Dilution Factor	Method Reporting Limit	Method Detection Limit	<b>Extraction</b> <b>Method</b>	Analysis Method
Dichlorodifluoromethane	ND	U			5.0	0.40		
Chloromethane	ND	U			5.0	0.056		
Vinyl Chloride	ND	U			5.0	0.067		
Bromomethane	ND	U			5.0	0.32		
Chloroethane	ND	U			5.0	0.32		
Trichlorofluoromethane (CFC 11)	ND	U			5.0	0.048		
1,1-dichloroethylene (1,1-DCE)	ND	U			5.0	0.37		
Dichloromethane (Methylene								
Chloride)	ND	U			5.0	0.11		
trans-1,2-Dichloroethene	ND	U			5.0	0.050		
1,1-Dichloroethane (1,1-DCA)	ND	U			5.0	0.051		
Chloroform	ND	U			5.0	0.63		
1,1,1-Trichloroethane (TCA)	ND	U			5.0	0.051		
Carbon Tetrachloride	ND	U			5.0	0.26		
Benzene	0.08				5.0	0.055		
1,2-Dichloroethane (EDC)	ND	U			5.0	0.39		
Trichloroethene (TCE)	ND	U			5.0	0.072		
1,2-Dichloropropane	ND	U			5.0	0.053		
Bromodichloromethane	ND	U	μg/l	1	5.0	0.056	none	624
2-Chloroethyl Vinyl Ether	ND	U			10	0.12		
Toluene	0.1				5.0	0.063		
1,1,2-Trichloroethane	ND	U			5.0	0.075		
Tetrachloroethene (PCE)	ND	U			5.0	0.085		
Dibromochloromethane	ND	U			5.0	0.081		
Chlorobenzene	ND	U			5.0	0.039		
Ethylbenzene	ND	U			5.0	0.053		
Bromoform	ND	U			5.0	0.11		
1,1,2,2-Tetrachloroethane	ND	U			5.0	0.083		
1,3-Dichlorobenzene	ND	U			5.0	0.071		
1,4-Dichlorobenzene	ND	U			5.0	0.073		
1,2-Dichlorobenzene	ND	U			5.0	0.086		
Acrolein <sup>†</sup>	ND	U			50	2.3		
Acrylonitrile <sup>†</sup>		U			10	0.28		
cis-1,3-Dichloropropene	ND	U			5.0	0.036		
trans-1,3-Dichloropropene	ND	U	1		5.0	0.048		
Bis(chloromethyl) Ether <sup>††</sup>	ND	U			10	10		
This compound is unstable under normal	الممصطنان	na Aana	· CDA Mat	had CO	1 audaliaaa	the renerte	بر مینامیر ام	

This compound is unstable under normal conditions. As per EPA Method 624 guidelines, the reported value was an estimate.

†† This compound is searched for as a tentatively identified compound.

Table 6 StarKist Samoa Effluent Priority Pollutant Semi-Volatile Analysis, June 2012								
Constituent		Result Notes (see Table 7)	nuits	ctor	Method Reporting Limit	Method Detection Limit	Extraction Method	Analysis Method
N-Nitrosodimethylamine	ND	U		4	100	6.8		
Bis(2-chloroethyl) Ether	ND	U		4	40	1.5		
Phenol	220	)=, D		4	40	1.8		
2-Chlorophenol	ND	U		4	40	1.7		
Bis(2-chloroisopropyl) Ether	ND	U		4	40	1.5		
Hexachloroethane	ND	U		4	40	1.1		
N-Nitrosodi-n-propylamine	ND	U		4	40	2.1		
Nitrobenzene	ND	U		1	10	0.36		
Isophorone	ND	U		1	10	0.35		
2-Nitrophenol	ND	U		1	10	0.35		
2,4-Dimethylphenol	ND	U		1	10	1.1		
Bis(2-chloroethoxy)methane	ND	U		1	10	0.31		
2,4-Dichlorophenol	ND	U		1	10	0.29		
1,2,4-Trichlorobenzene	ND	U		1	10	0.32		
Naphthalene	ND	U		1	10	0.31		
Hexachlorobutadiene	ND	U	μg/l	1	10	0.22	3520C	625
4-Chloro-3-methylphenol	ND	U		1	10	0.48		
Hexachlorocyclopentadiene	ND	U		1	10	0.58		
2,4,6-Trichlorophenol	ND	U		1	10	0.19		
2-Chloronaphthalene	ND	U		1	10	0.43		
Acenaphthylene	ND	U		1	10	0.29		
Dimethyl Phthalate	ND	U		1	10	0.71		
2,6-Dinitrotoluene	ND	U		1	10	0.27		
Acenaphthene	ND	U		1	10	0.27		
2,4-Dinitrophenol	ND	U		1	25	1.0		
4-Nitrophenol	ND	U		1	25	2.3		
2,4-Dinitrotoluene	ND	U		1	10	0.26		
Fluorene	ND	U		1	10	0.23		
4-Chlorophenyl Phenyl Ether	ND	U		1	10	0.26		
Diethyl Phthalate	0.43	J		1	10	0.33		
4,6-Dinitro-2-methylphenol	ND	U		1	25	2.3		

Table 6								
StarKist Samoa Effluent Priority Pollutant Semi-Volatile Analysis, June 2012								
Constituent	Result	Result Notes (see Table 7)	Units	ctor	Method Reporting Limit	Method Detection Limit	Extraction Method	Analysis Method
N-Nitrosodiphenylamine	ND	U		1	10	0.34		
1,2-Diphenylhydrazine	ND	U		1	10	0.23		
4-Bromophenyl Phenyl Ether	ND	U		1	10	0.35		
Hexachlorobenzene	ND	U		1	10	0.27		
Pentachlorophenol (PCP)	ND	U		1	25	0.38		
Phenanthrene	ND	U		1	10	0.24		
Anthracene	ND	U		1	10	0.33		
Di-n-butyl Phthalate	ND	U		1	10	0.46		
Fluoranthene	ND	U		1	10	0.45		
Benzidine	ND	U		1	50	29		
Pyrene	ND	U		1	10	0.47		
Butyl Benzyl Phthalate	ND	U	μg/l	1	10	0.55	3620C	625
3,3'-Dichlorobenzidine	ND	U		1	25	0.48		
Benz(a)anthracene	ND	U		1	10	0.25		
Chrysene	ND	U		1	10	0.40		
Bis(2-ethylhexyl) Phthalate	1.2	2J		1	10	0.34		
Di-n-octyl Phthalate	ND	U		1	10	0.38		
Benzo(b)fluoranthene	ND	U		1	10	0.27		
Benzo(k)fluoranthene		U		1	10	0.32		
Benzo(a)pyrene	ND	U		1	10	0.37		
Indeno(1,2,3-cd)pyrene	ND	U		1	10	0.45		
Dibenz(a,h)anthracene	ND	U		1	10	0.41		
Benzo(g,h,i)perylene	ND	U		1	10	0.41		

Table 7. Data Qualifiers for StarKist Samoa June 2012 Priority Pollutant Analysis							
Constituents	Symbol	Interpretation					
	=	Value of constituent detected above the MRL with no qualifiers.					
	ND	Constituent was not detected					
General	U	The compound was analyzed, but was not detected at or above the MRL/MDL (Method Reporting Limit or the Method Detection Limit)					
	J	The result is an estimated concentration that is less than the MRL but greater than or equal to the MDL					
	N/A	Not Applicable					
	*	The result is an outlier. See case narrative (Attachment 1).					
Conventional	Н	The holding time for this test is immediately following sample collection. The samples were analyzed as soon as possible after receipt by the laboratory					
Metals	N	The Matrix Spike sample recovery level is not within control limits.  See case narrative (Attachment 1).					
Overtice	i	The MRL/MDL has been elevated due to a chromatographic interference					
Organics	*	The result is an outlier. See case narrative (Attachment 1).					

The reported result is from a dilution.

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12

# ATTACHMENT 1

**Laboratory Results** 

(Provided on CD-ROM)